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(54) Title: **OLEFIN POLYMERIZATIONS USING IONIC LIQUIDS AS SOLVENTS**

(57) **Abstract:** A process for making polyolefins is disclosed. At least one olefin is polymerized using a single-site catalyst, an optional activator, and an ionic liquid. The ionic liquid helps to increase catalyst lifetime and activity, particularly for late transition metal catalysts. Polymer products separate cleanly from the highly polar ionic liquid, making isolation and purification simple. The ionic liquid is easily recycled. Versatile and radically different from the usual nonpolar organics, ionic liquids are an exceptional choice as solvents for single-site catalyzed olefin polymerizations.



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OLEFIN POLYMERIZATIONS USING IONIC LIQUIDS AS SOLVENTS

FIELD OF THE INVENTION

5 The invention relates to a process for polymerizing olefins. In particular, the invention relates to olefin polymerizations performed in the presence of a "single-site" catalyst and an ionic liquid.

BACKGROUND OF THE INVENTION

10 Interest in single-site (metallocene and non-metallocene) catalysts continues to grow rapidly in the polyolefin industry. These catalysts are more reactive than Ziegler-Natta catalysts, and they produce polymers with improved physical properties. The improved properties include narrow molecular weight distribution, reduced low molecular weight extractables,
15 enhanced incorporation of α -olefin comonomers, lower polymer density, controlled content and distribution of long-chain branching, and modified melt rheology and relaxation characteristics.

 Traditional metallocenes commonly include one or more cyclopentadienyl groups, but many other ligands have been used. Putting
20 substituents on the cyclopentadienyl ring, for example, changes the geometry and electronic character of the active site. Thus, a catalyst structure can be fine-tuned to give polymers with desirable properties. Other known single-site catalysts replace cyclopentadienyl groups with one or more heteroatomic ring ligands such as boraaryl (see, e.g., U.S. Pat. No.
25 5,554,775), pyrrolyl, indolyl, (U.S. Pat. No. 5,539,124), or azaboroliny groups (U.S. Pat. No. 5,902,866).

 Single-site catalysts based on "late" transition metals (especially those in Groups 8-10, such as Fe, Ni, Pd, and Co) and diimines or other ligands have sparked considerable research activity because of the unusual
30 ability of these catalysts to incorporate functionalized comonomers or to give branched polyethylenes without including a comonomer. See, for example, U.S. Pat. Nos. 5,714,556 and 5,866,663 and PCT international applications

WO 96/23010, WO 98/47933, and WO 99/32226. Unfortunately, the activity of late transition metal catalysts is often less than desirable, probably because of their low electrophilicity.

Like most organic reactions, olefin polymerizations are often performed with the aid of an organic solvent, which is typically an aromatic or aliphatic hydrocarbon (e.g., toluene, hexanes). As ubiquitous as organic solvents are, they have inherent limitations. For example, most organic solvents are flammable. Many are toxic. Most have significant vapor pressure, which often gives them an objectionable odor. Organic solvents are often poor at dissolving transition metal catalysts. In addition, most common organic solvents are now regulated as VOCs (volatile organic compounds), with specific limits on how much can be released into the atmosphere. Organic solvents are normally liquids over a fairly narrow temperature range, which limits their utility. Separation of organic solvents from the desired reaction products is often challenging. Disposal costs provide yet another insult.

Recently, "ionic liquids" have emerged as an environmentally friendly alternative to organic solvents in separations and various organic reactions (see Chem. & Eng. News, Jan. 4, 1999, p. 23, and Aug. 24, 1998, p. 12). Ionic liquids are salts that are liquid over a wide temperature range, including room temperature. They are nonvolatile, nonflammable, thermally stable, highly solvating yet non-coordinating, and they are good solvents for many organic and inorganic substances.

Ionic liquids typically have a bulky organo-ammonium, phosphonium, or sulfonium cation, and a non-coordinating complex anion (such as hexafluorophosphate, tetrafluoroborate, or tetrachloro-aluminate). 1,3-Dialkylimidazolium salts have been thoroughly studied.

Ionic liquids have been reported as useful "solvents" in extractions with supercritical CO₂ (see Nature 399 (6 May 1999) 28) and in electrochemical applications (see, e.g., U.S. Pat. No. 5,827,602). They have also found utility in various organic reactions including catalytic hydrogenation (Chemtech (Sept. 1995) 26), olefin dimerization or

oligomerization (see U.S. Pat. No. 5,550,304 and J. Chem. Soc., Chem. Commun. (1990) 715), Diels-Alder reactions (U.S. Pat. No. 5,892,124), olefin metathesis (U.S. Pat. No. 5,675,051), hydroformylation of olefins (U.S. Pat. No. 6,025,529), alkylations (U.S. Pat. Nos. 5,824,832 and 5,994,602),
5 Friedel-Crafts reactions (J. Org. Chem. 51 (1986) 480 and Chem. Commun. (1998) 2097) and butene polymerization in the absence of an added catalyst (U.S. Pat. No. 5,304,615). Despite their versatility, ionic liquids have not been suggested for use as solvents for single-site catalyzed olefin polymerizations.

10 In sum, there is a continuing need for better, more environmentally friendly olefin polymerization processes. In particular, olefin polymerizations catalyzed by single-site catalysts, especially those based on late transition metals, would benefit from new ways to boost catalyst activity. Ideally, the process would avoid the volatility, toxicity, and flammability concerns of
15 organic solvents, yet would allow simple, economical isolation of polyolefins.

SUMMARY OF THE INVENTION

The invention is an olefin polymerization process. The process comprises polymerizing one or more olefins in the presence of a single-site
20 catalyst, an optional activator, and an ionic liquid. In a preferred process of the invention, the catalyst incorporates a transition metal from Groups 6 to 8.

Ionic liquids are excellent solvents for single-site catalyzed olefin polymerizations. Their high dielectric constants help to stabilize cationically active species, thereby increasing catalyst lifetime and activity, particularly
25 for late transition metal catalysts. Polymer products separate cleanly from the highly polar ionic liquid, making isolation and purification simple. Ionic liquids are easily recovered and reused. Moreover, ionic liquids provide an alternate reaction medium that permits great control over product selectivity. In short, ionic liquids are an exceptional choice as solvents for olefin
30 polymerization reactions catalyzed by single-site catalysts.

DETAILED DESCRIPTION OF THE INVENTION

The process of the invention comprises polymerizing one or more olefins in the presence of a single-site catalyst, an optional activator, and an ionic liquid.

5 The catalyst is an organometallic complex. It is "single site" in nature, i.e., it is a distinct chemical species rather than a mixture of different species. Single-site catalysts, which include metallocenes, typically give polyolefins with characteristically narrow molecular weight distributions ($M_w/M_n < 3$) and good, uniform comonomer incorporation.

10 The organometallic complex includes a Group 3 to 10 transition metal or lanthanide or actinide metal, M. More preferred complexes include a Group 4 to 8 transition metal. The process of the invention is particularly well-suited to complexes that contain "late" transition metals, i.e., a metal from Groups 6 to 8, i.e., chromium, manganese, iron, cobalt, nickel, and
15 elements directly below these on the Periodic Table.

The organometallic complex optionally includes one or more additional polymerization-stable, anionic ligands. Examples include substituted and unsubstituted cyclopentadienyl, fluorenyl, and indenyl, or the like, such as those described in U.S. Pat. Nos. 4,791,180 and 4,752,597.
20 Suitable polymerization-stable ligands include heteroatomic ligands such as boraaryl, pyrrolyl, indolyl, quinoliny, pyridinyl, and azaborolinyl as described in U.S. Pat. Nos. 5,554,775, 5,539,124, 5,637,660, and 5,902,866. Suitable polymerization-stable ligands include indenoindolyl anions such as those described in PCT publication WO 99/24446. The organometallic complex
25 also usually includes one or more labile ligands such as halides, alkyls, alkaryls, aryls, dialkylaminos, or the like. Particularly preferred are halides, alkyls, and alkaryls (e.g., chloride, methyl, benzyl). A variety of other kinds of ligands are particularly useful with late transition metals, including, for example, N,N'-diaryl-substituted diazabutanes and other imines as
30 described in U.S. Pat. Nos. 5,714,556 and 5,866,663.

The polymerization-stable ligands can be bridged. For instance, a $-\text{CH}_2-$, $-\text{CH}_2\text{CH}_2-$, or $(\text{CH}_3)_2\text{Si}$ bridge can be used to link two polymerization-

stable ligands. Groups that can be used to bridge the ligands include, for example, methylene, ethylene, 1,2-phenylene, and dialkyl silyls. Normally, only a single bridge is included. Bridging changes the geometry around the metal and can improve catalyst activity and other properties such as
5 comonomer incorporation.

An activator is optionally included. Suitable activators help to ionize the organometallic complex and activate the catalyst. Suitable activators are well known in the art. Examples include alumoxanes (methyl alumoxane (MAO), PMAO, ethyl alumoxane, diisobutyl alumoxane), alkylaluminum
10 compounds (triethylaluminum, diethyl aluminum chloride, trimethylaluminum, triisobutyl aluminum), and the like. Suitable activators include acid salts that contain non-nucleophilic anions. These compounds generally consist of bulky ligands attached to boron or aluminum. Examples include lithium tetrakis(pentafluorophenyl)borate; lithium tetrakis(pentafluorophenyl)-
15 aluminate, anilinium tetrakis(pentafluorophenyl)borate, and the like. Suitable activators also include organoboranes, which include boron and one or more alkyl, aryl, or aralkyl groups. Suitable activators include substituted and unsubstituted trialkyl and triarylboranes such as tris(pentafluorophenyl)borane, triphenylborane, tri-n-octylborane, and the
20 like. These and other suitable boron-containing activators are described in U.S. Pat. Nos. 5,153,157, 5,198,401, and 5,241,025.

The optimum amount of activator needed relative to the amount of organometallic complex depends on many factors, including the nature of the complex and activator, the particular ionic liquid used, the desired
25 reaction rate, the kind of polyolefin product, the reaction conditions, and other factors. Generally, however, when the activator is an alumoxane or an alkyl aluminum compound, the amount used will be within the range of about 0.01 to about 5000 moles, preferably from about 0.1 to about 500 moles, of aluminum per mole of M. When the activator is an organoborane or an
30 ionic borate or aluminate, the amount used will be within the range of about

0.01 to about 5000 moles, preferably from about 0.1 to about 500 moles, of activator per mole of M.

The polymerization is performed in the presence of an ionic liquid. Suitable ionic liquids are salts that exist in the liquid state at temperatures used to polymerize olefins. Preferred ionic liquids are liquids at and below
5 room temperature, and many are liquids at temperatures as low as about –100°C. Preferably, the ionic liquids consist of a bulky organic cation and a non-coordinating, complex inorganic anion. The anion is “non-interfering” with respect to the single-site catalyst, i.e., it does not prevent or significantly
10 inhibit the catalyst from effecting polymerization of the olefin.

A wide variety of ionic liquids suitable for use in the process of the invention have been described. For example, U.S. Pat. Nos. 5,827,602, 5,731,101, 5,304,615, and 5,892,124, disclose many suitable ionic liquids. Preferred cations are organo-ammonium, phosphonium, and sulfonium ions
15 such as pyridinium, imidazolium, tetraalkylammonium, trialkylsulfonium, tetraalkylphosphonium, and the like. Other heterocycles containing at least one quaternary nitrogen or phosphorus or at least one tertiary sulfur are also suitable. Exemplary heterocycles that contain a quaternary nitrogen include pyridazinium, pyrimidinium, oxazolium, and triazolium ions. Particularly
20 preferred cations because of their low cost, ease of preparation, and ready availability are N-alkylpyridinium and 1,3-dialkylimidazolium ions. By varying the number of carbons and branching on the alkyl chains of these cations, the melting range of the ionic liquid can easily be adjusted to a desirable value. Preferably, the alkyl chains have from 2 to 12 carbons, more
25 preferably from 4 to 10 carbons.

Suitable anions are complex inorganic anions that are “non-coordinating” with respect to the organic cation and “non-interfering” with respect to the cationically active species. On the whole, catalysts of the late transition metals will be active with a wider range of “non-interfering” anions
30 than will catalysts of the early transition metals. Many suitable anions are conjugate bases derived from protic acids having a pKa less than 4. (For example, a suitable anion is tetrafluoroborate, the conjugate base of

fluoroboric acid, which has $\text{pK}_a < -5$.) Other suitable anions are adducts of a Lewis acid and a halide, such as tetrachloroaluminate. Suitable anions include, for example, hexafluorophosphate, hexafluoroantimonate, tetrafluoroborate, tetrachloroborate, tetraarylborates, polyfluorinated
5 tetraarylborates, tetrahaloaluminates, alkyltrihaloaluminates, triflate (CF_3SO_3^-), nonaflate ($\text{CF}_3(\text{CF}_2)_3\text{SO}_3^-$), chloroacetate, trifluoroacetate, sulfate, nitrate, nitrite, trichlorozincate, dichlorocuprate, fluorosulfonate, triarylphosphine sulfonates (e.g., as disclosed in U.S. Pat. No. 6,025,529), and polyhedral boranes, carboranes, and metallacarboranes, and the like.

10 The amount of ionic liquid used is usually not critical and depends largely upon the type of process to be used. For example, a gas-phase process might require a relatively small amount of the ionic liquid, while a solution process performed using only the ionic liquid as a solvent might use a relatively large amount. Generally, the ionic liquid will be used in an
15 amount within the range of about 1 to about 100 wt.% based on the combined amount of ionic liquid, activators, and single-site catalyst.

If desired, a catalyst support such as silica or alumina can be used. However, the use of a support is generally not necessary and may be undesirable for practicing the process of the invention.

20 Olefins useful in the process of the invention are compounds having at least one polymerizable carbon-carbon double bond. Preferred olefins have a single carbon-carbon double bond. They include ethylene and C_3 - C_{20} α -olefins such as propylene, 1-butene, 1-hexene, 1-octene, and the like. Isoolefins (e.g., isobutene or isooctene) or cycloolefins (e.g., cyclohexene)
25 are suitable as are cyclic olefins (e.g., norbornene) and dienes (e.g., 1,3-butadiene). Some or all of the olefin can be replaced with an acetylenically unsaturated monomer (e.g., 1-octyne or 1-hexyne). Mixtures of olefins can be used. Ethylene and mixtures of ethylene with C_3 - C_{10} α -olefins are especially preferred.

30 Functionalized comonomers can be included provided that the comonomer also contains at least one polymerizable carbon-carbon double bond. Such functionalized monomers are used advantageously with late

transition metal catalysts. For example, the olefin polymerization can be conducted in the presence of a minor proportion of allyl alcohol, acrylic acid, hydroxyethylmethacrylate, or the like. Olefin polymers prepared by the process of the invention have recurring olefin units.

5 Many types of olefin polymerization processes can be used. Preferably, the process is practiced in the liquid phase, which can include slurry, solution, suspension, or bulk processes, or a combination of these. High-pressure fluid phase or gas phase techniques can also be used. The process of the invention is particularly valuable for solution and slurry
10 processes. Suitable methods for polymerizing olefins using the catalysts of the invention are described, for example, in U.S. Pat. Nos. 5,902,866, 5,637,659, and 5,539,124.

In one suitable process of the invention, a reactor is pre-conditioned with a solution of alkylaluminum compound in a volatile hydrocarbon. An
15 ionic liquid is then added, followed by the single-site catalyst and optional activator. Volatiles are removed, and then the reactor is heated to the desired reaction temperature and pressurized with the olefin to be polymerized. Olefin is fed on demand until the reaction is complete. The desired polyolefin product separates cleanly from the highly polar ionic
20 liquid.

In a preferred process of the invention, the single-site catalyst includes a "late" transition metal, i.e., a Group 6-8 transition metal. While late transition metal catalysts have been used with a variety of activators, their activities have often been lower than desirable. In addition, late
25 transition metal catalysts normally have little ionic character, particularly when used in the normal hydrocarbon solvent. The ionic liquid easily dissolves the catalyst and helps to stabilize it. In addition, it enhances the activity of the late transition metal catalyst (compared with the activity of the catalyst when used in a nonpolar organic solvent) by "solvating" the
30 cationically active species and its counterion.

The olefin polymerizations can be performed over a wide temperature range, such as about -100°C to about 280°C . A more preferred range is

from about 30°C to about 180°C; most preferred is the range from about 60°C to about 100°C. Olefin partial pressures normally range from about 15 psia to about 50,000 psia. More preferred is the range from about 15 psia to about 1000 psia.

5 Catalyst concentrations used for the olefin polymerization depend on many factors. Preferably, however, the concentration ranges from about 0.01 micromoles per liter (of reaction mixture) to about 100 micromoles per liter. Polymerization times depend on the type of process, the catalyst concentration, and other factors. Generally, polymerizations are complete
10 within several seconds to several hours.

 The process offers valuable advantages over known single-site catalyzed olefin polymerizations, particularly those performed with the aid of an organic solvent. As noted above, the high polarity of ionic liquids increases catalyst lifetime and activity, particularly for late transition metal
15 catalysts. Because the polymer products separate cleanly from the highly polar ionic liquid, isolation and purification are simple. Ionic liquids are easily recovered and reused.

 As a highly polar reaction medium, ionic liquids provide a radical alternative to the traditional nonpolar organic solvents. With ionic liquids,
20 catalysts need not be "bulked up" with organic ligands to achieve adequate solubility. Moreover, the kind of polymer product available should differ significantly from what can be made with nonpolar organics, and the product slate should expand considerably just by tuning the structure of the ionic liquid. Thus, ionic liquids provide enhanced control over product selection.
25 In short, ionic liquids are an exceptional choice as solvents for olefin polymerization reactions catalyzed by single-site catalysts.

 The following examples merely illustrate the invention. Those skilled in the art will recognize many variations that are within the spirit of the invention and scope of the claims.

30

EXAMPLE 1

Ethylene Polymerization Using an Ionic Liquid

A dry, deaerated 100-mL autoclave is charged with 1-butyl-3-methylimidazolium hexafluorophosphate (50 mL) and 0.091 grams of [(2,6-i-Pr₂PhN=CMe-CMe=N-2,6-i-Pr₂Ph)PdMe(NCMe)][SbF₆]. Ethylene is admitted to the autoclave until the pressure reaches 2.1 MPa. The reaction mixture is stirred at 24°C for 1.5 h. The reactor is depressurized, and the polymer product is separated from the ionic liquid.

EXAMPLE 2

Ethylene Polymerization Using an Ionic Liquid

A 1.7-L stainless-steel autoclave is flushed with isobutane (500 mL) and a scavenging amount of triisobutylaluminum. 1-Butyl-3-methylimidazolium hexafluorophosphate (100 mL) is transferred to the reactor, followed by bis(n-butylcyclopentadienyl)zirconium dichloride (0.4 mg, 0.001 mmol) and methylalumoxane (1 mmol), which is flushed into the reactor with isobutane (100 mL). The isobutane is removed by flashing at 80°C, leaving a "solution" of single-site catalyst, activator, and ionic liquid. The reaction mixture is kept at 80°C throughout the subsequent polymerization using external heating or cooling.

The reactor is pressurized to 150 psig with ethylene, and additional ethylene is fed on demand as the polymerization proceeds. After about 1 hour, the reactor is vented, and the reaction mixture is cooled to 30°C. Polyethylene, the expected reaction product, collects on the surface of the ionic liquid and is easily isolated. The ionic liquid portion can be used for a subsequent polymerization.

The preceding examples are meant only as illustrations. The following claims define the invention.

I claim:

1. A process which comprises polymerizing one or more olefins in the presence of a single-site catalyst, an optional activator, and an ionic liquid.
- 5 2. The process of claim 1 wherein the olefin is ethylene or a mixture of ethylene and an α -olefin.
3. The process of claim 1 wherein the catalyst includes a Group 3 to 10 transition, lanthanide, or actinide metal and a polymerization-stable anionic ligand.
- 10 4. The process of claim 3 wherein the metal is a Group 6 to 8 transition metal.
5. The process of claim 3 wherein the polymerization-stable ligand is selected from the group consisting of substituted and unsubstituted cyclopentadienyl, boraaryl, pyrrolyl, pyridinyl, quinolinyl, azaborolinyll, and
15 indenoindolyl.
6. The process of claim 1 wherein the activator is an alumoxane or an ionic borate or aluminate.
7. The process of claim 1 wherein the ionic liquid is a liquid at temperatures within the range of about 0°C to about 60°C.
- 20 8. The process of claim 1 wherein the ionic liquid is used in an amount greater than 5 wt.% based on the amount of polyolefin produced.
9. The process of claim 1 wherein the ionic liquid has the structure $[A]^+[X]^-$ where $[A]^+$ is an organoammonium, organosulfonium, or organophosphonium ion, and $[X]^-$ is a non-coordinating, complex anion
25 derived from a protic acid having a $pK_a < 4$.
10. The process of claim 9 wherein $[A]^+$ is selected from the group consisting of N-alkylpyridinium, 1,3-dialkylimidazolium, tetraalkylphosphonium, trialkylsulfonium, and tetraalkylammonium.
11. The process of claim 9 wherein $[X]^-$ is selected from the group
30 consisting of hexafluorophosphate, hexafluoroantimonate, tetrahaloborates, fluorosulfonate, triflate, nonaflate, and trifluoroacetate.

12. The process of claim 1 wherein the ionic liquid has the structure $[A]^+[X]^-$ where $[A]^+$ is an organoammonium, organosulfonium, or organophosphonium ion, and $[X]^-$ is a non-coordinating, complex anion produced by adding a halide ion to a Lewis acid.

5 13. The process of claim 12 wherein $[A]^+$ is selected from the group consisting of N-alkylpyridinium, 1,3-dialkylimidazolium, tetraalkylphosphonium, trialkylsulfonium, and tetraalkylammonium.

14. The process of claim 12 wherein $[X]^-$ is selected from the group consisting of tetrachloroaluminate, tetrabromoaluminate, ethyl
10 trichloroaluminate, and polynuclear anions derived from these.

15. A process which comprises polymerizing one or more olefins in the presence of a Group 6 to 8 transition metal-containing single-site catalyst, an optional activator, and an ionic liquid.

16. The process of claim 15 wherein the olefin is ethylene or a
15 mixture of ethylene and an α -olefin.

17. The process of claim 15 wherein the catalyst includes at least one polymerization-stable ligand selected from the group consisting of substituted and unsubstituted cyclopentadienyl, boraaryl, pyrrolyl, pyridinyl, quinolinyl, azaborolinyl, and indenoindolyl.

20 18. The process of claim 15 wherein the ionic liquid has the structure $[A]^+[X]^-$ where $[A]^+$ is an organoammonium, organosulfonium, or organophosphonium ion, and $[X]^-$ is a non-coordinating, complex anion derived from a protic acid having a $pK_a < 4$.

25 19. The process of claim 15 wherein the ionic liquid has the structure $[A]^+[X]^-$ where $[A]^+$ is an organoammonium, organosulfonium, or organophosphonium ion, and $[X]^-$ is a non-coordinating, complex anion produced by adding a halide ion to a Lewis acid.

30 20. A process which comprises polymerizing ethylene in the presence of a Group 6 to 8 transition metal-containing single-site catalyst, an optional activator, and an ionic liquid, wherein the ionic liquid has the structure $[A]^+[X]^-$ where $[A]^+$ is an organoammonium, organosulfonium, or organophosphonium ion, and $[X]^-$ is selected from the group consisting of:

(a) non-coordinating, complex anions derived from protic acids having a $pK_a < 4$; and (b) non-coordinating, complex anions produced by adding a halide ion to a Lewis acid.

INTERNATIONAL SEARCH REPORT

Int l Application No
PCT/US 01/06086

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08F10/00 C08F4/80 C08F4/70 C08F4/64

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	RICHARD T. CARLIN: "Complexation of Cp2MC12 in chloroaluminate molten salt: relevance to homogeneous Ziegler-Natta catalysis" JOURNAL OF MACROMOLECULAR CATALYSIS, vol. 63, 1990, pages 125-129, XP001025777 page 126, paragraph 2 - paragraph 3 ---	1-3,5,7, 8,12-14
X	US 6 037 442 A (PROULX GRANT) 14 March 2000 (2000-03-14) examples 1,2,7 --- -/--	1-5, 7-10, 12-16, 18-20

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

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INTERNATIONAL SEARCH REPORT

Int. Patent Application No.

PCT/US 01/06086

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	OLIVIER H ET AL: "NONAQUEOUS ROOM-TEMPERATURE IONIC LIQUIDS: A NEW CLASS OF SOLVENTS FOR CATALYTIC ORGANIC REACTIONS" CHEMICAL INDUSTRIES, NEW YORK, NY, US, vol. 68, 1996, pages 249-263, XP000938205 ISSN: 0737-8025 abstract page 252, line 1 -page 253, paragraph 1 page 258: Future Trends -----	1-4, 6-16, 18-20
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